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14. ABSTRACT

The goal of this research program was to develop a comprehensive, predictive, and detailed kinetic model of hydrocarbon combustion for aero propulsion simulations. Sensitivity analyses were performed to examine the influences of the uncertainty in binary diffusion coefficients on flame simulations. First-principles calculations were carried out to determine the molecular binary diffusion coefficients of H-He, H2-He, H-H2, and H-Ar gas mixtures. This study resulted in an updated transport property library commonly used in combustion simulations. A new class of radical-chain initiation reactions was discovered for the homogeneous oxidation of unsaturated hydrocarbons. This element of the study utilized advanced quantum chemistry tools, reaction rate theory, and the method of detailed kinetic modeling. This new class of initiation reactions was found to be critical to reaction model development. A detailed reaction model of C1-C4 fuel combustion was updated. The foundation of this model, namely the H2/CO sub-model, was revised completely and optimized. A new method, termed the Sensitivity Analysis Based (SAB) method, was developed for rapid model optimization. The method was shown to be far more efficient than the factorial design method used in previous kinetic model optimization efforts.

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DEVELOPMENT AND OPTIMIZATION OF A COMPREHENSIVE KINETIC MODEL OF HYDROCARBON FUEL COMBUSTION

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SUMMARY/OVERVIEW

The goal of this research program was to develop a comprehensive, predictive, and detailed kinetic model of hydrocarbon combustion for aeropropulsion simulations. To achieve this goal, research was conducted in several areas essential to the success of the model development. In the first area sensitivity analyses were performed to examine the influences of the uncertainty in binary diffusion coefficients on flame simulations. A first-principle calculation was carried out to determine the binary diffusion coefficients of H-He, H_2-He, H-H_2, and H-Ar. This study resulted in an updated transport property library commonly used in combustion simulations. In the second area a new class of radical-chain initiation reactions was discovered for homogeneous oxidation of unsaturated hydrocarbons. This element of the study utilized advanced quantum chemistry tools, reaction rate theory, and the method of detailed kinetic modeling. This new class of initiation reactions was found to be critical to reaction model development. In the third area, a detailed reaction model of C_1-C_4 fuel combustion had been actively updated. Notably the foundation of this model, namely the H_2/CO sub-model was completely revised and optimized. Lastly, a new method, termed as the Sensitivity Analysis Based (SAB) method, was developed for rapid model optimization. The method was shown to be far more efficient than the factorial design method used in previous kinetic model optimization efforts.

TECHNICAL DISCUSSION

1. A First-Principle Calculation for the Diffusion Coefficients of H-He, H_2-He, H-H_2, and H-Ar and An Updated Transport Library

Law and coworkers reported the laminar flame speeds of H_2-O_2-He mixtures in the pressure range of 1 to 20 atm. They showed that the flame speeds were severely over-predicted using the chemical reaction model of Mueller *et al.* and the SANDIA transport database, and the discrepancy becomes larger at higher pressures. Our sensitivity analysis showed that the laminar flame speed is sensitive not only to key reaction rate parameters, but it is equally sensitive to the binary diffusion coefficients of pairs like H-He, H-H_2, and H_2-He.

Prompted by the above study, we undertook a study with the aim of providing more accurate binary diffusion coefficients for pairs important to the H_2-O_2-He flames. We carried first-principle calculations for the diffusion coefficients of H-He, He-H_2, and H-H_2, over a wide temperature range. A similar calculation was performed for the diffusion coefficient of H-Ar.

Chapman-Enskog theory was used to obtain the binary, atom-atom diffusion coefficients in terms of the collision integral. The collision integrals were directly calculated by numerical integration using the literature potential functions for H-He and H-Ar. Second-order correction to the diffusion coefficient was made. For He-H_2 and H-H_2, we considered the influence of internal degrees of freedom on the scattering process and consequently the diffusion coefficients. The scattering problem was solved using the Close-Coupling method, which transforms the time-independent Schrödinger equation into a set of coupled second-order differential equations. These equations were integrated to obtain the scattering S-matrix. The energy-dependent cross-sections were then calculated from the S-matrix elements, and the diffusion cross-section was obtained by thermally averaging the energy-dependent cross-sections with a Boltzmann weighting factor and summing the contribution from each rotational transition.

Literature potential energy functions were carefully evaluated against various cross section data from molecular beam experiments and against our own quantum chemical CCSD(T)/aug-cc-PV*Z calculations. Reliable potential energy functions were then chosen for the computation of diffusion coefficients. Table 1 presents the diffusion coefficients, computed for H-He, H-Ar, and H-H_2 and compared to data directly measured for these pairs. The computed diffusion coefficients were found to be in good agreement with the data. Figures 1-3 show comparisons of the present calculations with those predicted by the Sandia TRANFIT and DRFM compilations. It is seen that the DRFM and TRANFIT predictions differ markedly from our first-principle results at high temperatures.

Using the H-He, He-H_2, and H-H_2 diffusion coefficients calculated above, we recomputed the flame speeds of H_2-O_2-He mixtures. The flame speeds were compared to the experimental data of Law and coworkers and those computed using the Sandia TRANFIT database. Figure 4 shows that no improvements were made for the prediction using the new diffusion coefficients. However, the remaining uncertainty can now be safely attributed to reaction kinetics, as described in Section 3.

Our study demonstrated that a semi-empirical approach to estimate the diffusion coefficient used by the TRANFIT and DRFM packages might not be adequate for a quantitative prediction of basic flame properties such as the laminar flame speed. Rather, the diffusion coefficients of many key pairs will have to be closely examined, case by case, to ensure the accuracy of these coefficients at high temperatures.

Following the conclusions reached above, the Sandia transport database was updated. Within the framework of Sandia PREMIX [5] and similar codes, implementing these updates is quite straightforward, even if diffusion coefficients are available for only a few pairs. The current updates are tabulated in Table 1. These diffusion coefficients were obtained from the potential functions directly calculated from high-level quantum chemistry calculations, and in many cases, compared to available experimental data.

To use these diffusion coefficients in flame modeling, the temperature dependence of binary diffusion coefficients at 1 atm was fitted, as in Ref. 1, by

$$\ln D_{ij} = d_0 + d_1 \ln T + d_2 \left(\ln T\right)^2 + d_3 \left(\ln T\right)^3,$$

where d_k (k=0,3) is the polynomial coefficient, tabulated in Table 2 for selected pairs. For the mixture-averaged transport formulation, the above polynomial is sufficient for flame simulations.

The multi-component transport formulation as well as the computation of thermal diffusion ratio in both transport formulations, however, requires the input of the ratios of collision integrals, i.e., $A_{ij}^* = \Omega_{ij}^{(2,2)} / \left(2\Omega_{ij}^{(1,1)} \right)$, $B_{ij}^* = \left(5\Omega_{ij}^{(1,2)} - \Omega_{ij}^{(1,3)} \right) / \left(3\Omega_{ij}^{(1,1)} \right)$ and $C_{ij}^* = \Omega_{ij}^{(1,2)} / \left(3\Omega_{ij}^{(1,1)} \right)$. These ratios are given for each pair in the following forms,
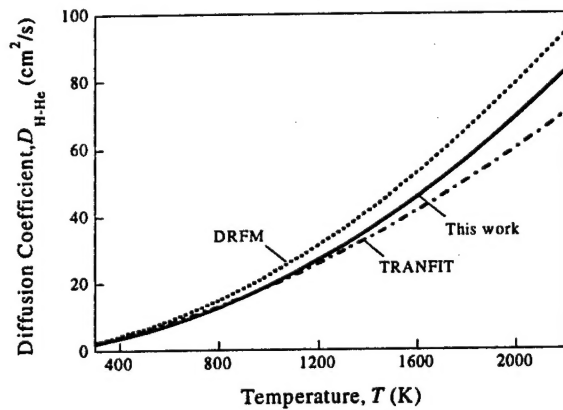
$$A_{ij}^* = a_0 + a_1 \ln T_{ij}^* + a_2 \left(\ln T_{ij}^* \right)^2 + a_3 \left(\ln T_{ij}^* \right)^3,$$

$$B_{ij}^* = b_0 + b_1 \ln T_{ij}^* + b_2 \left(\ln T_{ij}^* \right)^2 + b_3 \left(\ln T_{ij}^* \right)^3,$$

$$C_{ij}^* = c_0 + c_1 \ln T_{ij}^* + c_2 \left(\ln T_{ij}^* \right)^2 + c_3 \left(\ln T_{ij}^* \right)^3,$$

where a_k, b_k, and c_k (k=0,3) are the polynomial coefficients whose values are found in Table 1, and T_{ij}^* is the reduced temperature determined by the collision well depth ε_{ij} as $T_{ij}^* = kT / \varepsilon_{ij}$.
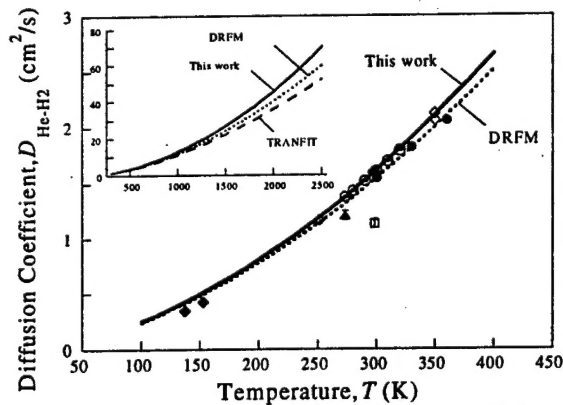
The above results are reported in Refs. 1-3.

Figure 1. Comparison of H-He diffusion coefficient computed in the present work with those predicted by Sandia TRANFIT and DRFM.
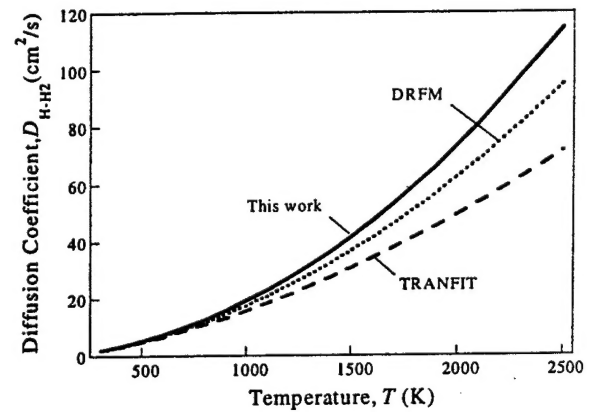
Figure 2. Comparison of H-H$_2$ diffusion coefficient computed in the present work with those predicted by Sandia TRANFIT and DRFM.

Figure 3. Comparison of H$_2$-He diffusion coefficient computed in the present work with experimental data and those predicted by Sandia TRANFIT and DRFM.
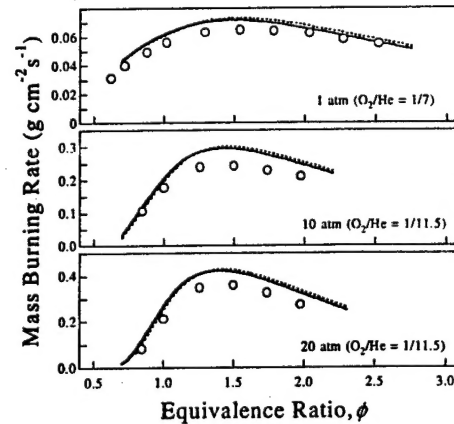
Figure 4. Experimental (symbols, Law and coworkers) and computed mass burning rate of H$_2$-O$_2$-He mixtures. Solid lines: computed with the Sandia TRANFIT database; dotted lines: computed with the diffusion coefficients of the present study.

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Table 1. Comparison of experimental and computed diffusion coefficients (cm^2/s) at 298 K and 1 atm.

Pair	Computed	Experimental	Pair	Computed	Experimental
H-He	2.22	$2.2 \pm 0.1, 2.7 \pm 0.1, 2.9 \pm 0.7$	H-Ar	1.35	$1.4 \pm 0.2, 1.4 \pm 0.1, 1.3 \pm 0.2,$
H-H$_2$	2.15	$2.1 \pm 0.1, 2.4 \pm 0.3, 2.2 \pm 0.2$			$1.5 \pm 0.3, 1.61 \pm 0.4$

Table 2 Summary of polynomial coefficients for updated binary diffusion coefficients and ratios of collision integrals

Pair	Diffusion coefficients, D_{ij}				A_{ij}^*			
	d_0	d_1	$d_2 \times 10^2$	$d_3 \times 10^3$	a_0	$a_1 \times 10$	$a_2 \times 10^2$	$a_3 \times 10^3$
H-He	-9.6699	2.1002	-7.7060	5.4611	0.93003	0.80150	-0.94733	0.63459
H-Ar	-9.0511	1.6161	-0.2878	1.3054	0.68819	1.53423	-1.76995	0.88796
H-H$_2$	-11.7498	3.1507	-25.7472	15.8916	0.68565	1.53390	-1.36735	0.32210
H-O$_2$	-11.0410	2.4043	-10.2797	5.3264	1.29254	-1.84989	4.27103	-2.60823
H-N$_2$	-13.2703	3.5187	-29.6649	16.4314	1.33865	-0.85454	0.92291	0.04406
H$_2$-He	-12.7513	3.4244	-28.4726	15.9317	0.59534	2.07809	-2.48477	1.00128
H$_2$-N$_2$	-10.9994	2.2026	-8.1155	4.4061	1.31648	-1.32021	2.41620	-1.20259
H$_2$-H$_2$	-9.9610	2.0560	-6.4977	4.1368	1.32209	-1.20749	2.20471	-1.05955

Pair	B_{ij}^*				C_{ij}^*			
	b_0	$b_1 \times 10$	$b_2 \times 10^2$	$b_3 \times 10^3$	c_0	$c_1 \times 10$	$c_2 \times 10^2$	$c_3 \times 10^3$
H-He	0.87638	1.02383	-1.48030	0.98804	1.06002	-0.59928	1.02650	-0.73451
H-Ar	0.69683	1.71580	-2.43568	1.36548	0.67027	1.14334	-1.50407	0.51876
H-H$_2$	0.67795	1.37471	-1.10587	0.16577	0.65119	0.82160	-0.43894	-0.27358
H-O$_2$	1.99270	-2.72201	2.05951	0.16444	1.27566	-2.27862	4.44995	-2.74619
H-N$_2$	-2.20300	15.91601	-25.33938	13.64477	1.27616	-2.25934	4.64183	-3.10151
H$_2$-He	0.67715	1.35792	-1.14253	0.18886	0.65192	0.83651	-0.44501	-0.25987
H$_2$-H$_2$	3.63140	-11.39793	16.94208	-8.12678	1.29811	-1.78141	2.95671	-1.70201
H$_2$-N$_2$	1.94230	-4.19106	6.71192	-3.36850	1.29073	-1.93012	3.39899	-1.96836

2. Initiation of Free-Radical Chain Reactions in Oxidation of Unsaturated Hydrocarbons

The initiation of free-radical chain reactions during homogeneous oxidation and ignition of hydrocarbon compounds is traditionally described by two types of reactions. The first is the C–H fission in the fuel molecule. The second is the hydrogen abstraction of fuel molecules by molecular oxygen. In most cases initiation reactions are overtaken by chain branching reactions at the very onset of reaction. For this reason they usually do not exhibit as large an influence as chain branching processes. On the other hand, an accurate prediction of the characteristics of fuel oxidation such as the shock-tube ignition delay cannot be made without adequately considering the nature and rates of initiation reactions.

A good example is the homogeneous oxidation of acetylene in shock tubes. It is well established that the initial radicals are produced from the reaction of acetylene and molecular oxygen, yet the nature of this reaction became known only until recently. Following the pioneering work of Kiefer and coworkers, we proposed that the initiation reactions during acetylene oxidation start with acetylene isomerization to vinylidene followed by the reaction of

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vinylidene with molecular oxygen. We showed that a detailed kinetic model of acetylene oxidation featuring this chain-initiation mechanism describes very well a variety of shock-tube ignition delay data reported for acetylene.

The conclusion of that study also opens up the possibility that there is a third type of initiation reactions for the oxidation of unsaturated fuels, namely, the isomerization or decomposition of the fuel molecule to a singlet carbene species followed by the reaction of carbene with molecular oxygen. In fact, many unsaturated hydrocarbons (e.g., acetylene, ethylene, propyne, and allene) can isomerize via 1,2-H shift to form singlet carbene species with threshold energy much smaller than that of C—H fission. If these carbene species are capable of reacting with molecular oxygen within their lifetime, they may provide a source of initial radicals to initiate chain reactions. In this work, we examine the viability of a chain initiation mechanism involving single carbene species in the homogeneous oxidation of representative unsaturated hydrocarbon compounds including ethylene, allene, propyne, and 1,3-butadiene. The work is of critical importance to a generalized understanding of the nature of radical-chain reactions during hydrocarbon combustion, and to the development of a comprehensive kinetic mechanism of hydrocarbon combustion.

We propose that the initial radicals in the homogeneous oxidation of ethylene, propyne, allene, and 1,3-butadiene are produced from two types of singlet species, vinylidene (H_2CC:) and propenylidene (CH_3CHC:), as the intermediates of the initial decomposition or isomerization of the fuel molecules, i.e., $C_2H_4 \rightarrow H_2CC$: $+ H_2$, aC_3H_4 and $pC_3H_4 \rightarrow CH_3CHC$:, and $1,3\text{-}C_4H_6 \rightarrow H_2CC$: $+ C_2H_4$, followed by H_2CC: $+ O_2 \rightarrow$ free radicals and CH_3CHC: $+ O_2 \rightarrow$ free radicals. Quantum chemistry calculations were carried out to estimate the thermochemistry of species that participate in these reactions and to explore the potential energy surfaces of selected reactions. The reaction steps were then included in a detailed kinetic model of C_2-C_4 fuel combustion. The validity of the initiation mechanism was verified by kinetic modeling of shock-tube ignition delay of ethylene, propyne, and allene, with and without the carbene chemistry. For every unsaturated fuels tested carbene reactions were found to produce initial free radicals at significantly faster rates than C—H fission and H-abstraction by molecular oxygen.

Thus we conclude that the initial radical pool during high-temperature, homogeneous oxidation of ethylene, propyne, allene, and 1,3-butadiene is produced by singlet carbene intermediates of initial fuel decomposition, followed by the rapid reaction of the carbene species with molecular oxygen. Combined with the findings of previous studies on the chain initiation mechanisms of acetylene, we conclude that the singlet carbene species plays a short-lived, yet significant role in the homogeneous oxidation of unsaturated hydrocarbons. The above results are reported in Ref. [4].

3. Development of a Comprehensive Reaction Mechanism of C_1-C_4 Fuel Combustion

In this work we extended the previously developed and validated reaction model of 1,3-butadiene combustion to *n*-butane, *i*-butane, 1-butene and 2-butene. In addition to mechanism development, there are two additional objectives in this study. First, we intend to address the question concerning the critical size of a well-optimized, small-hydrocarbon kinetic subset that can be used as secure foundations for extension to larger-hydrocarbon oxidation models. This question is motivated by our previous study which showed that a well-optimized C_1-C_2 kinetic subset cannot be used as a base set for the C_3 combustion model without re-optimizing the subset. Yet it is not clear whether there exists a critical kinetic subset larger than which a sequential optimization process can be conducted without having to re-optimize the critical subset when the combustion of a new hydrocarbon fuel is included in the comprehensive reaction

model. Second, in collaboration with Professors C. K. Law (Princeton) and C. J. Sung (Case Western Reserve), we have initiated a study of the laminar flame speed of fuel blends with a specific objective to examine the influence of kinetic coupling of fuel mixtures on laminar flame propagation. The initial fuel blend used in the investigation was the *n*-butane and ethylene mixture, which is representative of an alkane-alkene fuel blend.

A detailed reaction model was compiled, which consists of 81 species and 570 elementary reactions. Figure 3 presents the preliminary comparison between the experimental flame speeds and computational results of *n*-butane-air mixtures. The reaction model used in the computation was not optimized. Preliminary comparisons of the experimental data and modeling results for ethylene, 2-to-1, 1-to-1, and 1-to-2 mixtures of ethylene and butane, and butane flame speeds were also carried out.
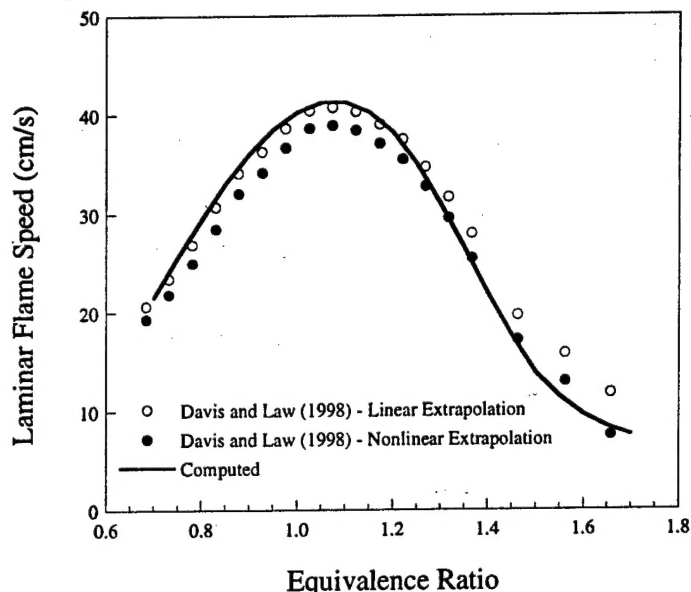
The above results are reported in Refs. 5 and 6.

Figure 5. Experimental and computed flame speeds of *n*-butane-air mixtures at the atmospheric pressure.

The reaction mechanism of H_2/CO oxidation is the kinetic foundation for the combustion of all hydrocarbons. In our previously compiled reaction mechanism, the H_2/CO submodel was based on the GRI-Mech. Over the last two or three years, there have been renewed interest in the rate constants of the key radical-chain termination reaction $H+O_2+M = HO_2+M$. Kinetic parameters newly made available show marked differences from those in early literature compilations. These new kinetic parameters gave us an urgent reason to re-examine the H_2-CO combustion model. In addition, the downward revision of the enthalpy of formation of OH may also exhibit a marked influence on the overall reaction kinetics of H_2 combustion. The current work was also motivated by the fact that the H_2-submodel of the GRI-Mech has not been optimized against a large body of H_2 combustion data.

The objectives of the present study are (1) to update the H_2-CO combustion reaction model on the basis of recent kinetic data, and (2) to optimize the H_2-CO model against available experimental data. Special attention has been placed on the capability of the model to predict ultra-lean H_2/air flames that correspond to a kinetics regime relevant to hydrocarbon ignition.

The revised, trial reaction mechanism consists of 14 species and 41 elementary reactions [7], and uses the revised diffusion coefficients of [1,3]. All rate constants have been re-evaluated and, when necessary, updated. The trial kinetic model was tested against over 60 sets of H_2/CO combustion experimental data, including shock-tube ignition delay time, laminar flame speed,

and the species profiles in turbulent flow reactors and in premixed burner-stabilized flames. Our trial model has also been tested against the oxidation of mixtures of H_2 and CO with generally good agreement.

The remaining uncertainties in the model were studied by a systematic optimization of model parameters with respect to a large set of target data, about 30 in all. These targets range from the global combustion properties of ignition delay and flame speed, to the more detailed species profiles during H_2 oxidation in flames and flow reactors. On the basis of sensitivity analyses, 27 rate parameters were considered as active. Response surfaces were developed using the methodology developed recently (to be discussed in Section 4). Optimization shows that an improvement of the trial reaction model could be achieved within the rate parameter uncertainty space. Compared to the trial model, the optimized reaction model predicts better the experimental data, as seen by the solid lines in Figures 6-10. Also shown in the figures are the predictions made using the Mueller-Kim-Yetter-Dryer (MKYD) reaction model (dashed lines).

In Figures 6-8, selected ignition delay comparisons show that reaction model predicts the experimental data reasonably well. The trial model yields the upward curvature towards lower temperatures as expected from the experimental observations. Figure 9 shows experimental and computed laminar flame speeds of H_2-air mixtures at the atmospheric pressure. The trial model is found to be in a close agreement with the experimental data. The trial model tends to over predict the H_2-O_2-He flame speeds at elevated pressures. The discrepancies are clearly due to kinetics as a previous study showed that the uncertainty in the transport coefficients cannot account for the observed differences. Figure 10 shows representative results obtained for the species profiles during H_2 oxidation in a turbulent flame reactor under three pressures, 0.3, 3.0, and 15.7 atm. It is seen that the model well captures the experimental features.

The currently optimized reaction model also resolves some of the stubborn cases that the MKYD model was not able to closely predict, as seen in Figures 6-8 and 10. In addition, the optimized model has been tested against new data on the extinction strain rates of ultra-lean H_2-air flames recently obtained in Professor Egolfopoulos's laboratory. The comparison results are satisfactory, as reported in [3].

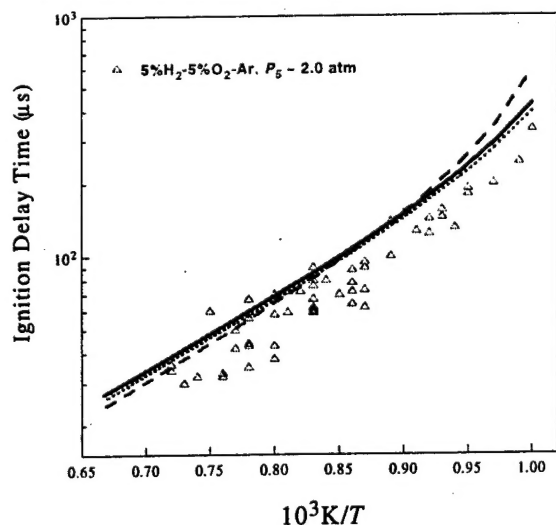The above results are reported in Ref. 8.

Figure 6. Experimental (symbols) [Cheng, R. K. and Oppenheim, A. K., *Combust. Flame* 58, 125-139 (1984).] and computed (line) ignition delay times of a 6.67%H_2 + 3.33%O_2 + 90%Ar mixture behind reflected shock waves ($P_5 \sim 1.9$ atm). Dotted line: trial model; solid line: optimized model; dashed line: MKYD model.
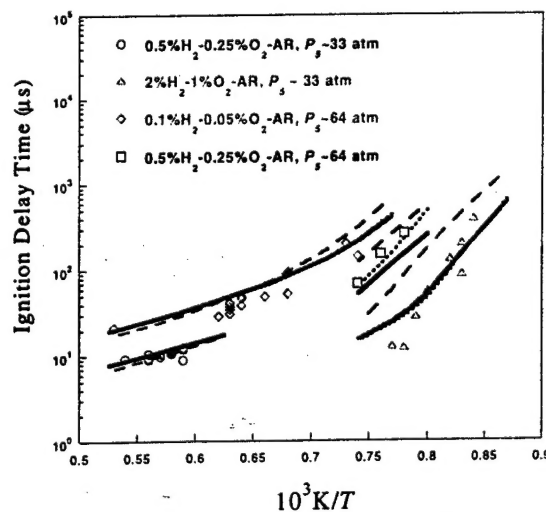
Figure 7. Experimental (symbols) [Peterson, E. L., Davidson, D. F., Rohrig, M. and Hanson, R. K., *20th Intl. Symp. Shock Waves*, 1996, pp. 941-946.] and computed (lines) delay times of maximum rate of [OH] absorption change for H_2-O_2-Ar mixtures behind reflected shock waves. Dotted line: trial model; solid line: optimized model; dashed line: MKYD model.
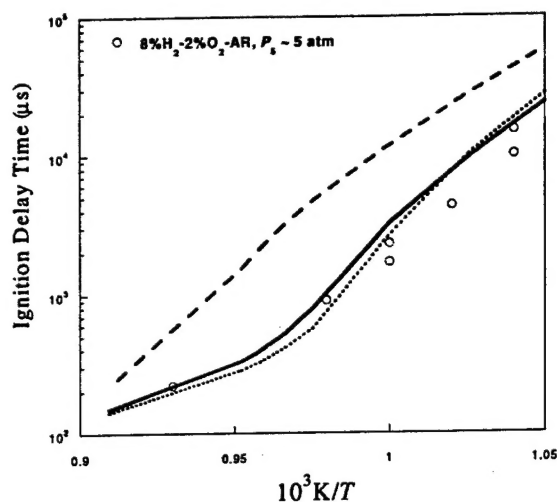
Figure 8. Experimental (symbols) [Skinner, G. B. and Ringrose G. H., J. Chem. Phys. 42, 2190-2192, (1965).] and computed (line) ignition delay times. Dotted line: trial model; solid line: optimized model; dashed line: MKYD model.
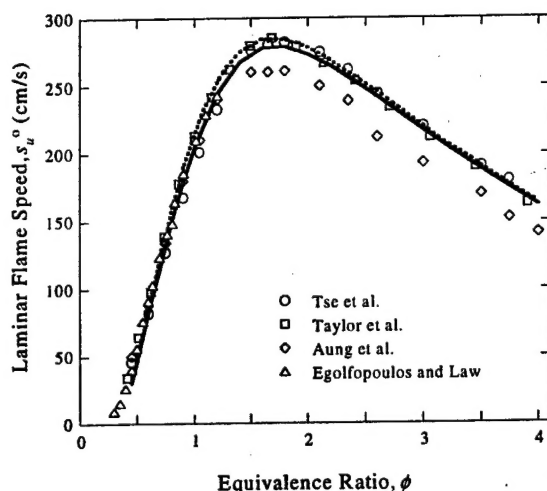

Figure 9. Experimental (symbols) [Tse, S. D., Zhu, D. L., and Law, C. K., *Proc. Combust. Inst.* 28, 1793-1800 (2000); Taylor, S. C., "Burning Velocity and the Influence of Flame Stretch," Ph.D. thesis, University of Leeds, 1991; Aung, K. T., Hassan, M. I., and Faeth, G. M., *Combust. Flame* 109, 1-24, (1997); Egolfopoulos, F. N. and Law, C. K., *Proc. Combust. Inst.* 23, 333-340 (1990)] and computed (line) laminar flame speed of H_2-air mixtures at the atmospheric pressure. Dotted line: trial model; solid line: optimized model.
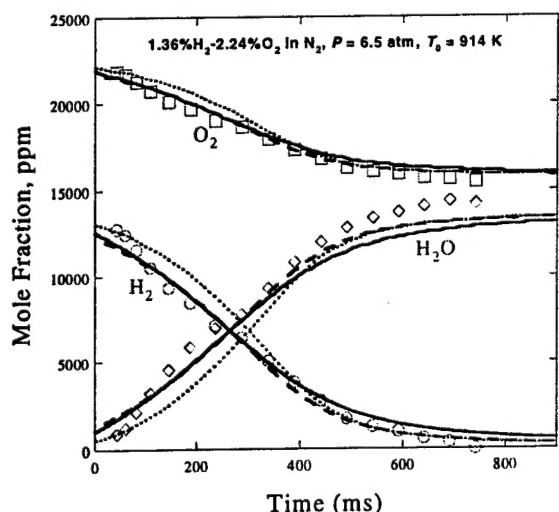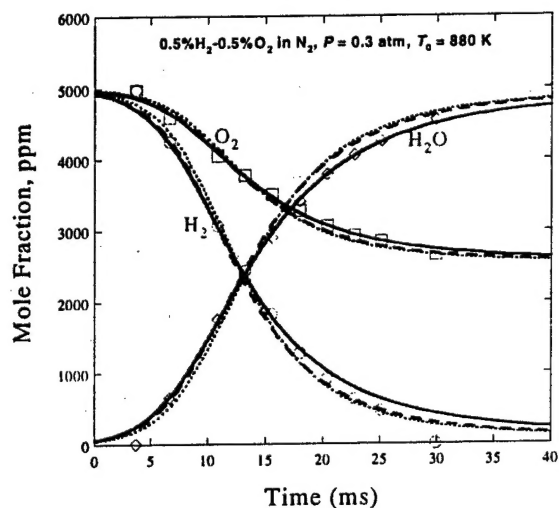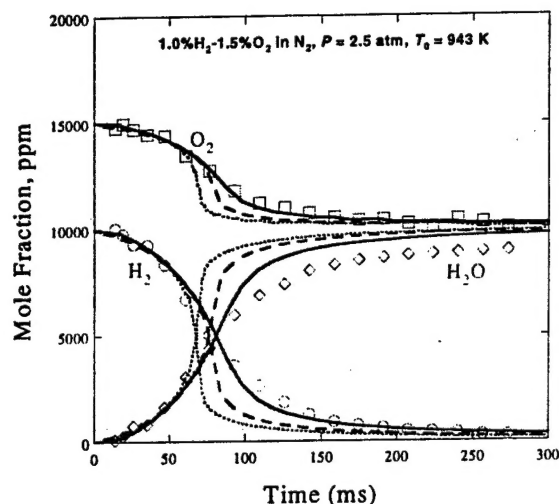

Figure 10. Experimental (symbols) [Mueller, M.A., Kim, T.J., Yetter, R.A. and Dryer, F. L. *Int. J. Chem. Kin.*, 31, 113 (1999).] and computed (lines) species profiles of H_2 oxidation in a turbulent flow reactor. Dotted line: trial model; solid line: optimized model; dashed line: MKYD model.

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Although the optimization results seem to be satisfactory, we realized that given the experimental uncertainty in the optimization targets, the optimization does not yield a unique, global minimum in the rate parameter uncertainty space. For this reason, the "optimized" model should be represented by a hypersurface on which every point (or rate parameter combination) is equally valid. We are currently developing a methodology that can express mathematically the hypersurface.

4. Development Of a New Response Surface Method for Mechanism Optimization

The optimization of a large reaction mechanism requires the minimization of an objective function given by the least squares differences of the computed and experimental flame responses. During minimization, thousands of least squares calculations are required. Direct flame solution to obtain flame response renders the optimization expansive and in most cases, prohibitive. To solve this problem, solution mapping was developed and used, for example, in the optimization of the GRI-Mech. In this method, a kinetic response surface is developed for each optimization target η, which expresses the target value as a simple function of reaction rate parameters. Usually, this response surface is expressed as a second-order polynomial,

$$\eta = a_0 + \sum_i^L a_i x_i + \sum_i^L \sum_{j \geq i}^L a_{ij} x_i x_j, \tag{1}$$

where L is the number of active rate parameters in that target, and x is the rate parameter k normalized by the uncertainty factor f, $x=\ln(k/k_0)/\ln(f)$, so when $x=0$, k is equal to the base rate parameter, k_0. Coefficients a were usually evaluated by regression of a factorial test. The factorial design method may become prohibitively expansive when L is large. The full factorial design requires 2^L+2L+1 numerical experiments. Fractional factorial design reduces the number of required numerical experiments at the expense of accuracy. For a flame-speed response surface with $L=13$, a $2^{13-4}+2\times13+1$ fractional factorial design requires 539 flame speed computations Therefore the development of response surfaces for flame speed can be a formidable task, and is usually a time hindrance during model optimization.

We developed a new method which is capable of producing a response surface at better than 1/10 of CPU cost with an accuracy which is comparable, if not better than, that from a factorial design analysis. This method is based on local sensitivity coefficients readily obtainable from available flame codes. Specifically, a combustion response was expanded about $x=0$. Comparing the terms in the Taylor expansion with eq. (1), we obtained expressions directly relating coefficients a_i with the first-order sensitivity coefficients, and a_{ij} with the second-order sensitivity coefficients, which were obtained by finite differencing the first-order sensitivity coefficients. The method proposed herein requires only $2L+1$ local sensitivity calculations, compared to $2^{L-M}+2L+1$ flame computations. Furthermore, these calculations also yield the third-order x_i^3 and $x_i^2 x_j$ terms.

Table 3 presents a comparison of the CPU costs and the mean, RMS, and maximum errors of representative response surfaces obtained by the sensitivity method and by fractional factorial design. It is seen that our sensitivity method yields 95 and 99% CPU savings for the two sample cases, yet the quality of the response surfaces is as good as those obtained with the factorial design method. Figure 11 presents a 45° angle diagonal plot of flame speeds predicted by response surfaces versus those from computational experiments. It is seen that the quality of the response surface obtained by the sensitivity method is excellent.

An automated computational code was developed for response surface analysis. The utility of this computational tool is obvious, in that it could reduce months of time devoted to response surface construction during mechanism optimization to a matter of few days.

The above results are reported in Refs. 9 and 10.

Table 3. CPUs and absolute errors (cm/s) of sample flame-speed response surfaces.

Method[a]	methane-air $\phi = 0.98, L = 10$		propane-air $\phi = 1.2, L = 13$	
	1	2	1	2
Number[b] of runs	21(S)	85(F)	27(S)	539(F)
Relative CPU	0.05	1.00	0.01	1.00
Mean error	0.2	0.3	0.5	0.3
RMS error	0.2	0.3	0.6	0.3
Maximum error	0.5	0.7	1.0	0.9

[a] (1) sensitivity method; (2) 2^{L-4} fractional factorial design. [b] "F" denotes the number of flame calculations. "S" denotes the number of sensitivity runs.
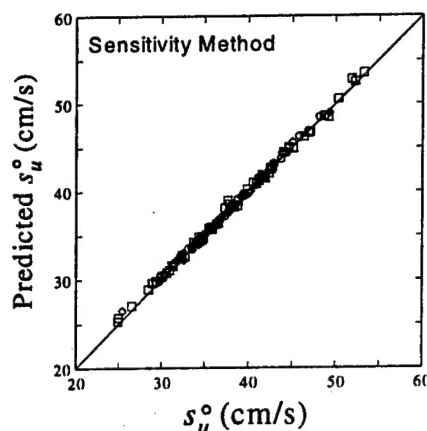
Figure 11. 45° angle diagonal plots of methane-air flame speeds ($\phi = 0.98$) predicted by the response surfaces as a function of the flame speed values obtained from computational experiments.

TECHNOLOGY TRANSFER

The following technology transition and transfer was made:

Performer: Dr. Hai Wang, University of Delaware, (302) 831-4464
　　　　　　Dr. C. K. Law, Princeton University, (609)-258-5271
Customer: Dr. Chris Montgomery, Reaction Engineering International, 77 West 200 South Suite 210, Salt Lake City, Utah 84101 (801-364-6925).
Result: Detailed ethylene reaction mechanism.
Application: CFD simulation of combustion in gas turbines.

Performer: Dr. Hai Wang, University of Delaware, (302) 831-4464
Customer: Dr. Meredith B. Colket, United Technologies Research Center, 411 Silver Lane, MS #29, East Hartford, Connecticut 06018 (860-510-7481)
Result: Computer Codes for Simulation of Transient Perfectly Stirred Reactors.
Application: Analysis of the Joint Strike Fighter (JSR) Augmentor design.

EXTRAMURAL-INTRAMURAL INTERACTIONS

Collaborative interactions have been initiated with Dr. Thomas Jackson's group. More specifically, UD had work closely with Dr. Dean Eklund of Taitech and to supply a simplified ethylene reaction mechanism for use in the simulation of gas turbine combustion. A discussion has been initiated with Dr. J. T. Edwards through Dr. Skip William concerning the involvement of UD in the development of kinetics for surrogate fuels of JP-8. UD also had close interactions and discussion with Dr. Skip Williams concerning the thermochemistry of ionic hydrocarbon species. At the request of Dr. Fred Schauer, UD supplied a revised transport database and its associated computer codes to assist the flame modeling work at the Wright-Patterson AFB.

PUBLICATIONS AND SELECTED CONFERENCE PRESENTATIONS (May 2001 – December 2003)

1. Middha, P., Yang, B., and Wang, H. "A first-principle calculation of the binary diffusion coefficients pertinent to kinetic modeling of hydrogen-oxygen-helium flames," *Proceedings of the Combustion Institute* **29**, pp. 1361-1369 (2002).

2. Yang, B., Middha, P. and Wang, H. "A theoretical study of binary diffusion coefficients of H-He and H-Ar at high temperatures," in *Chemical and Physical Processes of Combustion*, 2001 Fall Technical Meeting of the Eastern States Section of the Combustion Institute, Hilton Head, SC, December 2001, pp. 202-205.

3. Dong, Y., Holley, A. T., Andac, M. G., Egolfopoulos, F. N., Davis, S. G., Middha, P., and Wang, H. "Premixed extinction of H_2/air flames: Chemical kinetics and diffusion effects," *Proceedings of the Combustion Institute*, submitted, 2003.

4. Wang, H. "A new mechanism for initiation of free-radical chain reactions during high-temperature, homogeneous oxidation of unsaturated hydrocarbons: ethylene, propyne, and allene," *International Journal of Chemical Kinetics* **33**, pp. 698-706 (2001).

5. Hirasawa, T., Sung, C. J., Joshi, A., Yang, Z., Wang, H. and Law, C. K., "Determination of laminar flame speeds of fuel blends using digital particle-image velocimetry: ethylene, *n*-butane, and toluene flames," *Proceedings of the Combustion Institute* **29**, pp. 1427-1434 (2002).

6. Law, C. K., Sung, C. J., Wang, H., and Lu, T. F. "Development of comprehensive detailed and reduced reaction mechanisms for combustion modeling," *AIAA Journal* **41**, pp. 1629-1646 (2003).

7. Davis, S. G., Joshi, A. Wang, H., and Egolfopoulos, F. N. "A comprehensive and optimized kinetic model of H_2/CO combustion," Third Joint Meeting of the US Sections of the Combustion Institute, Chicago, March 2003, paper A8.

8. Davis, S. G., Joshi, A. V., Wang, H., and Egolfopoulos, F., "An optimized kinetic model of H_2/CO combustion," *Proceedings of the Combustion Institute*, submitted, 2003.

9. Davis, S. G., Mhadeshwar, A. B., Vlachos, D. G., and Wang, H. "A new approach to response surface development for detailed gas-phase and surface reaction kinetic model development and optimization," *International Journal of Chemical Kinetics* **36**, pp. 94-106 (2003).

10. Mhadeshwar, A. B., Wang, H., and Vlachos, D. G. "Thermodynamic consistency in microkinetic development of surface reaction mechanisms," *Journal of Physical Chemistry B* **107**, pp. 12721-12733 (2003).